MODIFICATIONS TO THE SURFACE CHEMISTRY OF LOW-RANK COAL-BASED CARBON CATALYSTS TO IMPROVE FLUE GAS NITRIC OXIDE REMOVAL

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Abstract

The effectiveness of carbons as low temperatures SCR catalyst will depend upon their physical and chemical properties. Surface functional groups containing oxygen are closely related to the catalytic activity of carbons. These groups are expected to change the interaction between the carbon surface and the reactants through a variation in adsorption and reaction characteristics. This paper presents a more detailed study of the effects of either gas-phase sulfuric acid or oxygen oxidation treatments on the catalytic NO reduction by low-rank coal-based carbon catalysts. Raw and treated carbons were characterized by N_2 and CO_2 surface areas, TPD and ash content. NO removal capacity of carbons was determined by passing a flow containing NO, H_2O, O_2, NH_3 and N_2 through a fixed bed of carbon at 150ºC and 4 s of residence time, the effluent concentration being monitored continuously during the reaction. The effects of varying the type and conditions of the treatment on the physicochemical features of carbons were studied. The gas-phase sulfuric acid treatment (corresponding to a first step SO_2 removal) markedly enhanced carbon activities for NO removal. On the contrary, oxygen oxidation enhanced NO removal capacity of chars to a lower extent. Therefore, the carbons studied could be used in a combined SO_2/NO removal process, because the use and regeneration of the carbon in the first step is beneficial for the performance in the second one.

KEYWORDS: Selective catalytic reduction; nitric oxide removal; coal-based carbon catalyst; surface modification.

Introduction

Nitric oxide is an important pollutant formed during the combustion of fossil fuels. It is oxidized in the atmosphere and reacts with other air pollutants causing photochemical air pollution (smog) and contributing to acid precipitation [1].

Significant reduction of NO_x emissions has been achieved by modification in combustion systems (burner and furnace design), but new stringent regulations should require the application of flue gas clean-up technologies. There are several studies in the literature (cited in the Introduction of ref. 2) concerning the role of carbons in direct reduction of NO. The possibility of using carbons in the role of catalyst for selective catalytic reduction (SCR) as catalyst or catalyst support and the use of activated carbons for NO removal by adsorption has been extensively studied as well. The SCR is the only flue gas denitrification technique so far that has proven to be very effective. It has been successfully commercialized and applied on a large scale [3]. During the SCR process, carbons and activated carbons can be used as catalyst in the SCR unit at lower temperatures than those used with conventional catalysts. The removal of NO by reaction with NH_3 in the presence of O_2 to produce N_2 follows the general equation:

$$4NO + 4NH_3 + O_2 \rightarrow 4\,N_2 + 6H_2O \qquad (1)$$

The effectiveness of carbons as low temperature SCR catalyst will depend upon their physical and chemical properties related to their origin and ways of production.

The adsorbent properties of carbons are usually dependent on their surface areas and appropriate pore size distributions. Besides physical characteristics, carbon surface chemistry (the presence of functional groups) is also very significant in determining the behavior of carbons. Especially, surface functional groups containing oxygen are closely related to the catalytic activity of carbons. These groups are expected to change the interaction between the carbon surface and the reactants through a variation of

adsorption and reaction characteristics [4-9]. Although the determination of the number and nature of these surface structures began more than half a century ago, the precise nature of the functional groups is not entirely established [10]. The estimates obtained by investigators using a number of experimental techniques differ considerably due to the complexity of carbon surface difficult to reproduce. However, the results concur in concluding that there might be several types of oxygen functional groups, conferring to carbons an acid-base character. The acidic groups include carboxyl, lactone and hydroxyl functionalities. Carbon basic properties are believed to arise from two different types of active sites; the existence of pyrone-type and chromene-type structures [11, 12] was postulated to account for the basic nature of the carbon surface. Carbons free of oxygen may also have basic sites arising from delocalized electrons [13].

The study of the chemistry of these surfaces involves indirect methods of investigation and the most commonly used are acid-base titration and temperature programmed desorption (TPD). Both methodologies are extensively reported in the literature [10, 14-16].

Previous work [17] has shown that the activity of low-rank coal-based carbons for NO reduction from flue gas is influenced by the presence of oxygen in the gas-phase and on the carbon surface. This paper presents a more detailed study of the effects of different surface treatments on the NO reduction of low-rank coal-based carbons.

The novelty of this work is the non-conventional modifications to surface chemistry. The target of the research is to explore the possibility of sulfuric acid generated in SO_2 abatement changing the surface chemistry of carbons after its removal.

A correlation between changes in the surface chemistry due to the treatment and NO removal performance is found. The changes of the physical structure due to these

treatments are also discussed.

Experimental

Samples. Two low-rank coal-based carbons (labeled S8 and S9) were used in this research. These carbons were synthesized by carbonization of a lignite in nitrogen atmosphere. Samples labeled S8A and S9A correspond to steam activated carbons S8 and S9, respectively, at the following activation conditions: 700ºC, 4 h and 10 g H_2O/min. Sample S8A1 correspond to steam activation of sample S8 at the following activation conditions: 600ºC, 2 h, 6 g H_2O/min. Sample S8A2 correspond to steam activation of sample S8 at the following activation conditions: 700ºC, 6 h, 12 g H_2O/min. Sample S8A4 correspond to steam activation of sample S8 at the following activation conditions: 700ºC, 2 h, 12 g H_2O/min

S9 sample was oxidized at 200ºC of temperature with a flow of 1 l/min either air or 3%O_2 in nitrogen. These samples were called S9ox21 and S9ox3, respectively.

The surface of some of these samples were modified by treatment with sulfuric acid in a non-conventional chemical activation procedure. A gas mixture containing SO_2-O_2-H_2O-N_2 is passed through a fixed bed containing 30 g of sample at 100ºC of temperature. The removal of the SO_2 from the gas mixture occurs by the formation of sulfuric acid that remains in the carbons. The amount of sulfuric acid formed can be controlled by the difference between the SO_2 inlet and outlet concentrations (measured continuously). This acid is thereafter removed from the carbon surface by thermal treatment at 400ºC of temperature in inert atmosphere, according to the reaction:

$$2H_2SO_4 + C \rightarrow 2SO_2 + CO_2 + 2H_2O \qquad (2)$$

The amount of sulfuric acid added to each sample and thereafter removed from it (expressed as mg) is shown in brackets in the reference of the acid-treated samples. A complete list of the samples studied is given in Table 1.

Characterization. The determination of the ash content of the samples studied was carried out according to ASTM standards for coal and coke.

Surface areas were determined with N_2 at 77K and CO_2 at 273K. The Brunauer-Emmet-Teller (BET) equation was applied to N_2 adsorption isotherms and the Dubinin-Radushkevich (DR) equation to CO_2 adsorption data. The meso and macropore volume values were taken from the Barret-Joyner-Halenda curves (BJH) calculated from N_2 adsorption data. The range of pore size diameters covered by the BHJ calculations was from about 17 to 3000 Å. The micropore volume values were obtained from CO_2 isotherm.

Temperature-programmed desorption (TPD) experiments followed by gas chromatography allow the determination of CO and CO_2 evolved at each temperature up to 1100ºC in inert atmosphere. In a typical run, 0.5 g of char was placed in a quartz tube reactor under a stream of argon flowing through at 30 cm^3/min. The sample was heated at 10ºC/min to 1100ºC.

More detailed experimental procedures are described elsewhere [17-19].

NO removal. The NO capacity removal of the different samples was tested in an experimental installation described elsewhere [17]. It consists of a fixed bed reactor of a inner diameter of 17 mm, devices for the preparation of the gas mixtures, temperature control and on-line analyses of the gas concentrations. The reactor was provided with a bypass which allows to measure each gas concentration before starting an experiment (a scheme of the experimental installation is shown in ref.17).

Experimental conditions to carry out this test were: a flow of 0.5 l/min containing 1000 ppmv of NO, 6% (v/v) of O_2, 10% (v/v) H_2O, 1500 ppmv NH_3 and N_2 as remainder, 150ºC of reaction temperature and 15 g of carbon. NO effluent concentration is monitored continuously during the reaction. The reaction results are described in terms

of conversion as %NO conversion = $[(NO_{in}-NO_{out})x100]/NO_{in}$.

Results and discussion

NO removal capacity tests. The variation in NO conversion with exposure time at 150ºC for series S8 samples is shown in Figure 1 and for series S9 in Figure 2.

The NO conversion was nearly 30% just after the initial contact between the char and the gas mixture for parent S8 and S9 samples, and it was maintained 20 hours after. The de-NO_x activities of S8 and S9 samples further treated with gas-phase sulfuric acid are also shown in Figure 1 and 2, respectively. Increasing the amount of sulfuric acid used in the treatment of the samples markedly enhanced the catalytic activity of the product char.

The conversion of NO on the acid-treated samples decreased from nearly 100% to different levels of conversion after a initial period of time ranging from 30 min to 2 h. High activities of some of the samples studied, i.e. samples S9A(1800) and S8A(2000) were maintained for the next 20 h. These activities are comparable to those shown by a commercial active carbon from Merck tested at the same experimental conditions, which exhibit a NO conversion of 80%. Sample S9A(1800) was tested under the NO removal capacity conditions for one week, and the catalytic activity was maintained at the conversion level corresponding to steady state.

Some selected samples were characterized after NO removal tests. Porous structure and carbon content were similar (under experimental error) to fresh samples (before NO removal experiments).

For comparison purposes, Table 1 show the conversion at steady state, the corresponding reaction rate for the steady state zone and the amount of NO removed after 20 h of experiment.

Porous structure. The N_2 and CO_2 surface area values of the samples, S_{N2} and S_{CO2},

respectively, are given in Table 2. This Table also reports the volume of macropores+mesopores and the volume of micropores as well as the ash content of the samples. The values of S_{N2}, S_{CO2} and pore volumes reported in Table 2 were normalized to the ash content of parent samples for comparison purposes. It can be seen that surface areas obtained from adsorption of CO_2 at 273K are always higher than those obtained from N_2 adsorption at 77K. These differences are indicative of pore constrictions at the entrance of the micropores. The differences become smaller as the severity of acid treatment increases, indicating an opening of the microporosity. This fact can be explained in terms of the carbon consumption according to reaction (2). Pore volume data shown in Table 2 are consistent with these results.

As can be deduced from Table 2, neither S_{CO2} nor S_{N2} correlate with the NO removal capacity of chars studied. Illan-Gomez et al. [20] found that the NO reduction activity of 10 carbons covering a wide range of surface area and pore size distributions correlate well with the N_2 BET surface area. In that work, authors concluded that at the temperatures studied all of the available surface area of the carbons was effective for the reaction and that accessibility problems due to diffusional limitations were not significant.

On the other hand, Ahmed et al. [21] did not find out correlation between NO conversion and physical properties such as BET surface area and pore size distribution. They used four commercial activated carbon samples synthesized from three different raw materials.

These contradictory findings [20, 21] indicate that not only the physical features but also chemical characteristics are responsible of the catalytic properties of the carbons.

Surface chemistry. Different studies have shown that the activity of carbons for NO conversion is influenced by the carbon surface. Singoredjo et al. [5] modified activated

carbons with nitrogen and oxygen containing organic compounds, followed by pyrolysis and CO_2 activation, and studied low-temperature SCR of NO with NH_3 at temperatures between 110 and 280ºC. An increase in NO reduction activity was attributed to the creation of stable C-O complexes.

Mochida et al. [22] reported that the mechanism of reduction of NO with NH_3 on carbon is reaction between ammonia on the acidic or dehydrogenative site and nitric oxide adsorbed on the oxidative site of the carbon surface. Different surface functional groups were introduced in that study by different chemical treatments.

Chemical activation is usually limited to woody precursors. Much of the literature is concerned with $ZnCl_2$ activation, and there have been relatively few studies on the synthesis of activated carbons from wood using other chemical reagents. The application of chemical activation to coals has been still more limited. A patent awarded to Carborundum [23] describes a process for the production of activated carbon from subbituminous coal using acid reagents (5 wt% of concentrated H_2SO_4, H_3PO_4 or HCl).

In our case, the modification of surface chemistry of the carbons studied to obtain different amounts of surface functional groups is achieved with sulfuric acid treatment (and consequent creation of “oxidative sites”) that activates the carbon for NO reduction. This enhancement of catalytic activity of acid-treated samples can be observed in Figure 3, where the amount of NO removed by the different samples is plotted against the amount of sulfuric acid added. It can be seen that there is a good correlation between the severity of the treatment and the catalytic activity (OX points are referred to parent chars).

This chemical treatment with sulfuric acid is not a conventional chemical activation, because the sulfuric acid comes from the removal of SO_2 over the carbons in a first step. A control of the SO_2 removed in this first step, gives the amount of sulfuric acid that has

been in contact with the carbon before it is removed from it. After removal, sulfur content of the chemically activated samples was determined, and no increase of this parameter was observed respect to the non-activated samples. This acid treatment produces remarkable amounts of oxygen functionalities, and a considerable portion of these could react with the ammonia present in the gas mixture to produce nitrogen functionalities, according to Fujitsu et al. [7]. Such structural changes in surface functionalities are reflected in the profiles of CO and CO_2 evolution during temperature-programmed desorption run, that are shown in Figure 4 and 5 for S9 samples. The amounts desorbed and the temperatures at which these gases were released have been found to be characteristic of various oxygen complexes. In general, it is agreed that the most important surface groups in order of decreasing acidity are: carboxylic acids, carboxylic anhydrides, carboxyl-carbonates, lactones, lactols, phenolic hydroxyl and quinonic carbonyl groups. It has been proposed that CO_2-yielding complexes like carboxylic acids, anhydrides and lactones are mainly responsible for the acidic character of carbon rather than the CO-yielding complexes like phenolic and quinonic groups. The complexes yielding CO_2 have been shown to decompose typically over a range of temperatures starting at 150ºC and exhibiting desorption maxima at 450 and 650ºC, and two types of chemically or energetically different entities were invoked. Whereas carboxylic acids have been proposed to be predominantly responsible for the low-temperature peak, the high-temperature CO_2 evolution has been attributed to carboxylic anhydrides. Similarly, the CO-yielding groups have been divided into two distinct groups which have CO evolution maxima at 650 and 900ºC.

The profiles of CO and CO_2 of the oxidized S9 sample are qualitatively similar to those found in the other oxidized samples of series S8, and also similar to those reported form other activated carbons oxidized with different treatments [24]. The TPD patterns

indicate that surface groups yielding oxygen evolved almost completely below 1000ºC. From TPD data, it is evident that the surface of S9A(1800) sample has the most acidic character among the carbons investigated from S9 series. Significant amounts of CO_2-yielding acidic groups are introduced onto the surface of the S9 sample as a result of the sulfuric acid treatment. The desorption of considerable amounts of CO from this carbon sample implies the decomposition of weakly acidic groups like phenols and quinones.

The peak or shoulder presented at 400ºC in CO_2 TPD profile has been observed in other oxidized activated carbons [24] and might be due either to the decomposition of some surface carboxyl groups, as suggested by the carbonization studies of model compounds. Thus benzoic acid decomposes round 400ºC [25]. These carboxyl groups seem to be also present in the S9 parent sample, but to a minor extent, exhibiting a shoulder at lower temperature. CO_2 peaks corresponding to the maximum amount evolved shift to different temperatures depending on the samples considered. Parent char S9 and oxygen-oxidized samples present the maximum of the peak at 625ºC and acid-oxidized samples at 700ºC. The thermal stability and the amount of the CO_2-yielding oxygen surface complexes increase with acid treatment.

The CO profiles of sample S9 shows a single and quite symmetric peak centered at about 800ºC, probably due to carbonyl groups and/or quinone-like structures which are thermally more stable than phenolic and /or hydroquinone groups. This maximum is shifted to around 900ºC in the acid-oxidized sample S9A(1800) because of the increase of the stability or surface complexes.

Oxygen-oxidized samples, S9ox3 and S9ox21, exhibit two CO desorption peaks: the maximum at 800ºC corresponding to that of parent sample and a small peak that appears at lower temperature, that comes from the decomposition of carbonyl groups in α-substituted ketones and aldehydes, as suggested by Surygala et al. [26].

Therefore, from TPD experiments, it can be deduced that carboxyl groups are formed during oxidation and that some of them are adjacent, and yield anhydride groups during the experiment. There is also some evidence of the formation of lactone groups as well as other CO-evolving groups such as phenol, carbonyl, hydroquinone and quinone-like structures. It is also shown that there are surface differences between acid-oxidized samples and oxygen-oxidized ones, not only in the amount of CO and CO_2 evolved but also in the oxygen-surface groups introduced by the treatment.

The total amount of CO and CO_2 desorbed from each sample is shown in Table 3 normalized to the ash content of the parent sample of each serie. These data are consistent with the observation, that is, both strongly and weakly acidic groups were introduced on parent samples as a result of oxidizing treatment. As seen in Table 3, the amounts of CO and CO_2 desorbed from the activated carbon were maximized by treatment with sulfuric acid. In comparison, much smaller amount of carbon oxides were desorbed from air or 3% O_2 oxidized samples.

The oxygen content of the samples shown in Table 3 is obtained from the amounts of CO and CO_2 evolved. It can be seen that S8 sample can fix a higher amount of oxygen than S9 sample. This fact could be related with differences in surface area of the original samples [25].

The use of infrared spectroscopy at DRIFT mode would give additional information on functional groups. However, the high ash content of the samples studied (particularly the presence of clays) interferes the study of oxygen functional groups. The demineralization of the samples would solve this problem, however the NO removal performance of demineralized samples was different to respect original sample. In this case, we prefer to use the original samples for this research and work will be done only using demineralized samples.

General discussion. . It is difficult to correlate the catalytic activity for NO removal of the samples studied with the type of oxygen surface complexes. The enhancement reduction of NO due to the introduction of new oxygen functional groups can be understood in terms of production of active sites, either by directly reaction NO, NH_3 or O_2, and also providing hydrophilic sites for H_2O adsorption. Therefore, an increase in the total amount of fixed surface groups on the chars could be correlated with NO-removal activity of carbons.

Figure 6 show the relationship among the total amount of CO and CO_2 evolved in a TPD experiment, the amount of sulfuric acid added to the samples and NO removal capacity of both S8 and S9 series samples. In the range of 20-40 cc/g of CO and CO_2 yielding groups, the amount of NO removed by the chars studied is low and corresponds to no sulfuric acid addition. From 40 cc/g to round 60 cc/g of CO and CO_2 yielding groups there is an important increase in the amount of NO removed by samples, this fact corresponding to an increase in the amount of sulfuric acid added. Finally, from this last point the increase in the NO removal capacity of samples is lower than in the intermediate range of CO and CO_2 yielding groups. In this way, it can be stated from Figure 6 that surface groups introduced by acid treatment enhance NO catalytic activity, particularly in the intermediate values of the $CO+CO_2$ (cc/g) range studied. This range also corresponds to an intermediate range of the amount of sulfuric acid added, i.e. both aspects follows a similar trend.

In conclusion, it was established that modification of low-rank coal-based carbons via sulfuric acid activation markedly enhanced the carbons' activities for NO removal and there is a good correlation between both aspects. Oxygen-oxidation of samples also enhance the NO removal capacity of carbons but to a lower extent than acid-oxidized samples. It can be deduced that an appropriate sample for NO removal can be tailored

by introduction of a fixed amount of surface groups.

Moreover, it has been demonstrated that the use of these carbons in the removal of SO_2 in a first step is better than the use of fresh carbons for the NO removal. So, it can be concluded that these carbons could be used in a combined SO_2/NO removal process.

Further research will be done in order to determine which of these surface groups are more beneficial for NO removal.

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Figure Captions

Figure 1. Reaction profiles of NO conversion over S8 serie. 1. S8; 2. S8(250); 3. S8A1(1000); 4. S8A4(1200); 5. S8A2(1400); 6. S8A(2000).

Figure 2. Reaction profiles of NO conversion over S9 serie. 1. S9; 2. S9ox3; 3. S9(400); 4. S9ox21; 5. S9A(1800).

Figure 3. Relationship between amount of sulfuric acid added and the amount of NO removed by S8 and S9 series.

Figure 4. Profiles of CO_2 evolution during temperature programmed desorption of S9 sample and its modified forms.

Figure 5. Profiles of CO evolution during temperature programmed desorption of S9 sample and its modified forms.

Figure 6. Relationship between amount of CO and CO_2 desorption in a TPD run, amount of sulfuric acid added and amount of NO removed by chars in a dynamic experiment.

Table 1. NO removal capacity of the chars studied.

Sample	Amount of NO removed after 20 h (mg NO/g char)	Conversion (%)	Reaction rate (mmol s/g char)
S8	12.1	30	3.0×10^{-5}
S8(250)	17.1	40	4.9×10^{-5}
S8A1(1000)	24.5	58	6.7×10^{-5}
S8A4(1200)	30.3	81	9.3×10^{-5}
S8A2(1400)	31.2	80	9.5×10^{-5}
S8A(2000)	37.7	90	12.0×10^{-5}
S9	12.0	30	2.9×10^{-5}
S9(400)	18.0	42	5.1×10^{-5}
S9A(1800)	32.5	85	9.6×10^{-5}
S9(ox3)	13.4	31	3.9×10^{-5}
S9(ox21)	18.7	44	5.5×10^{-5}

Table 2. BET and DR surface areas and ash content of the samples studied.

Sample	$S_{N2}^{(1)}$ m^2/g	$S_{CO2}^{(1)}$ m^2/g	$V^{(1)}_{macro+meso}$ cm^3/g	$V^{(1)}_{micro}$ cm^3/g	Ash %
S8	80	381	0.062	0.170	31.9
S8(250)	74	352	0.053	0.158	32.0
S8A1(1000)	77	365	0.066	0.166	34.0
S8A4(1200)	155	393	0.110	0.176	36.0
S8A2(1400)	198	397	0.152	0.180	40.0
S8A(2000)	298	349	0.227	0.156	42.5
S9	64	389	0.036	0.170	32.4
S9(400)	55	350	0.054	0.156	32.5
S9A(1800)	305	399	0.218	0.177	43.0
S9(ox3)	69	374	0.054	0.184	32.4
S9(ox21)	97	380	0.058	0.171	32.4

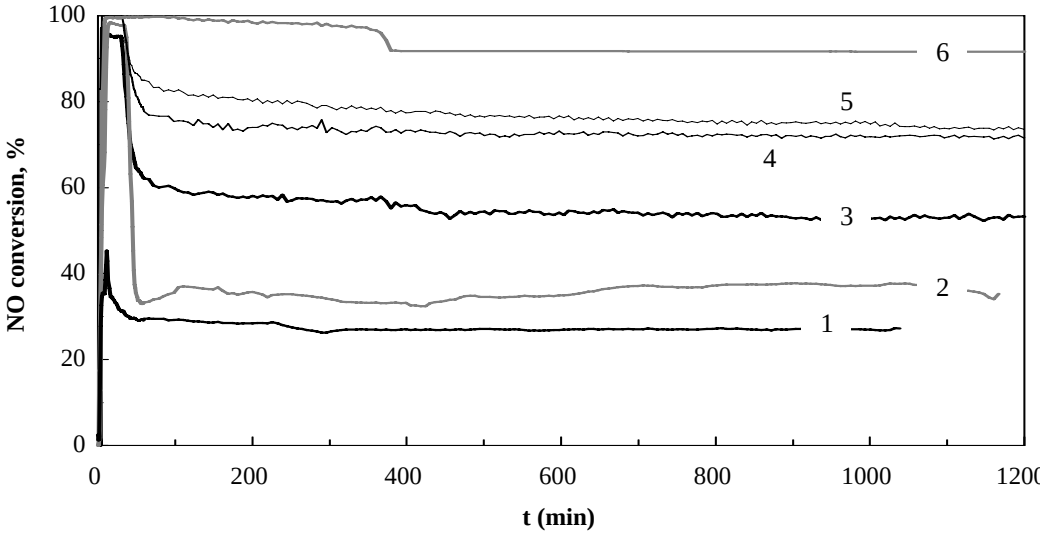
(1) normalized to the ash content of parent chars

Table 3. Concentrations of CO and CO_2-yielding groups of samples studied.

Sample	$CO^{(1)}$		$CO_2^{(1)}$		$O^{(2)}$
	mmol/g	cm^3/g	mmol/g	cm^3/g	%
S8	0.71	16.02	0.36	8.35	2.29
S8(250)	1.34	30.08	1.23	27.54	6.08
S8A1(1000)	1.32	29.58	1.09	24.37	5.60
S8A4(1200)	1.54	32.96	1.12	23.93	6.05
S8A2(1400)	1.61	33.02	1.05	21.48	5.94
S8A(2000)	2.63	53.02	1.58	32.30	9.26
S9	0.49	10.71	0.36	7.69	1.94
S9(400)	1.03	22.86	0.65	14.65	3.73
S9A(1800)	2.14	42.90	1.00	20.05	6.62
S9(ox3)	0.80	18.11	0.49	11.30	2.85
S9(ox21)	0.98	21.96	0.74	16.50	3.94

(1) normalized to the ash content of parent chars

(2) from the amount of CO and CO_2.


NO conversion, %
t (min)
100
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60
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200
400
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6
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4
3
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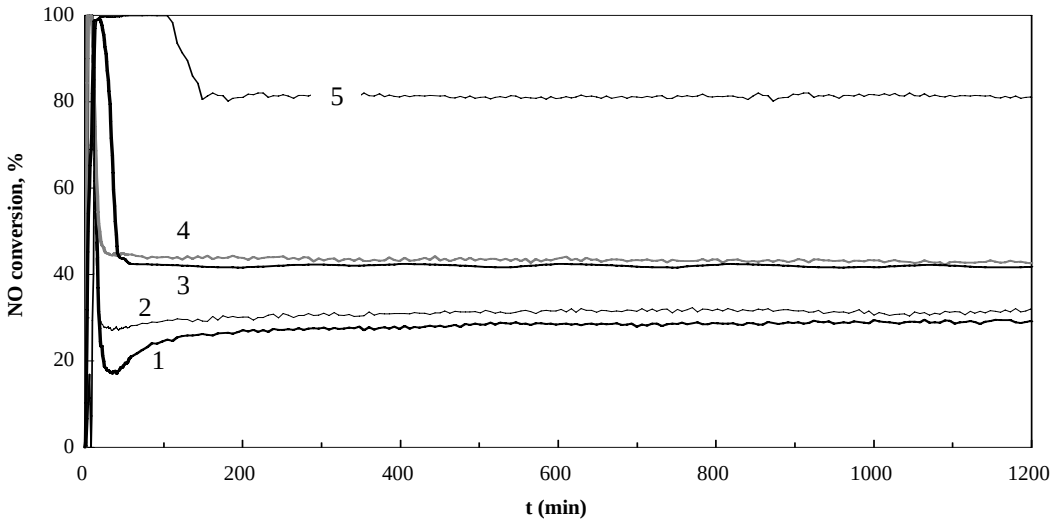
1

Figure 1


NO conversion, %
t (min)
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20
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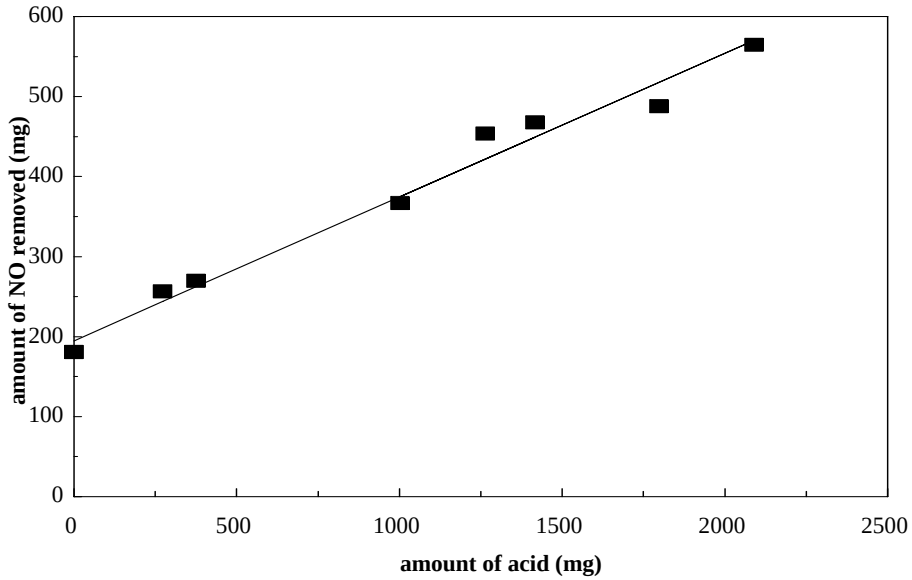
Figure 2


600
500
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300
200
100
0
amount of NO removed (mg)
0
500
1000
1500
2000
2500
amount of acid (mg)

Figure 3

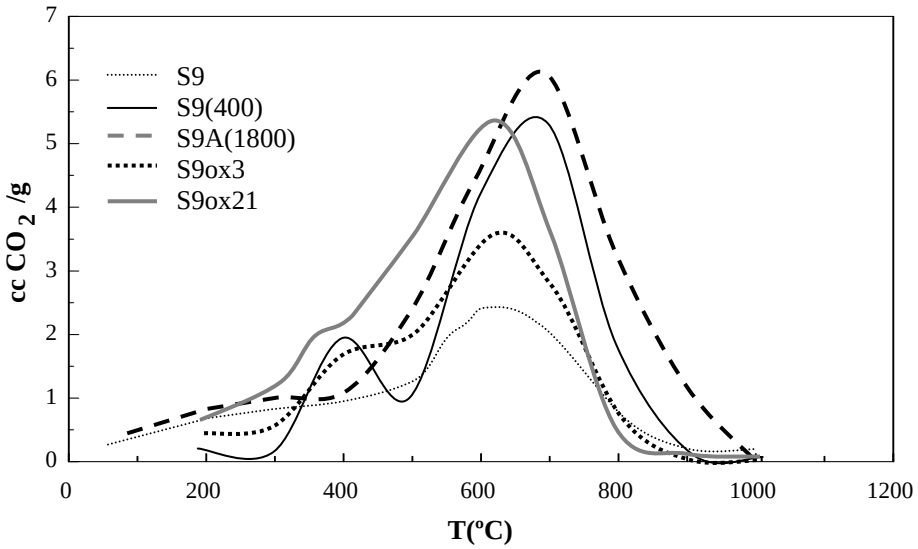
S9
S9(400)
S9A(1800)
S9ox3
S9ox21
cc CO 2 /g
T(ºC)
0
1
2
3
4
5
6
7
0
200
400
600
800
1000
1200

Figure 4

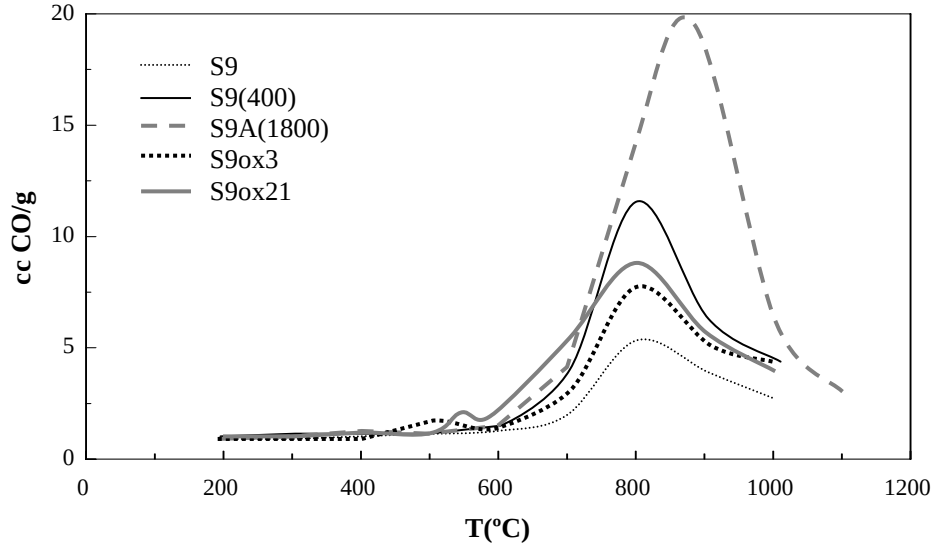
S9
S9(400)
S9A(1800)
S9ox3
S9ox21
cc CO/g
T(ºC)
0
5
10
15
20
0
200
400
600
800
1000
1200

Figure 5

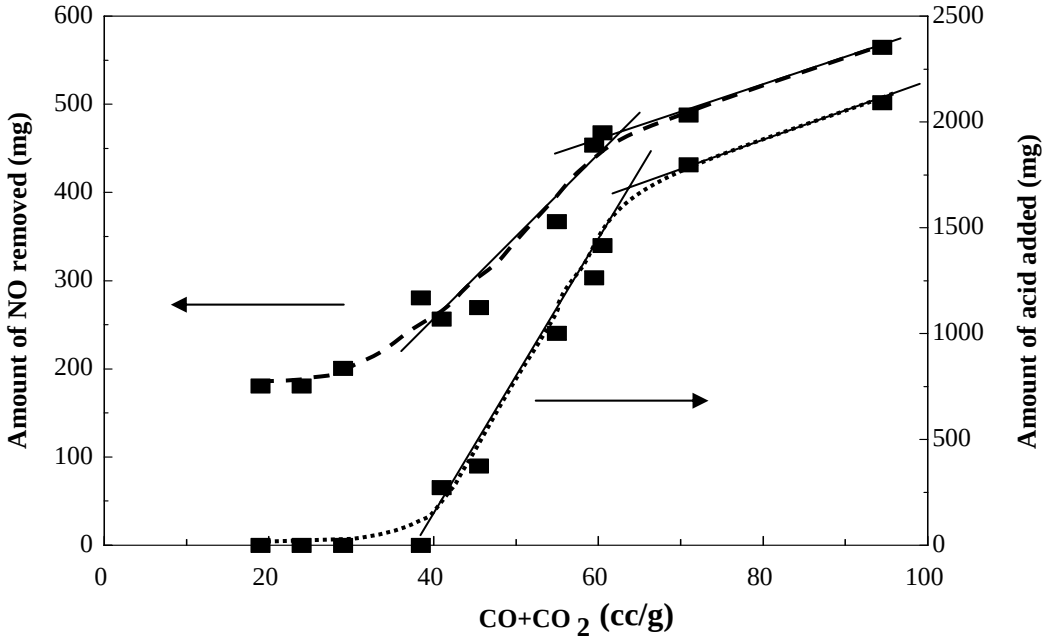
Amount of NO removed (mg)
Amount of acid added (mg)
CO+CO 2 (cc/g)
0
100
200
300
400
500
600
0
500
1000
1500
2000
2500
0
20
40
60
80
100

Figure 6